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SAFETY OF REDUCED LIQUID VOLUMES IN FUEL TANKS OF ROAD VEHICLES USING ALCOHOL FUELS

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Étude sur la sécurité par la réduction du volume de liquide contenu dans le réservoir des véhicules routiers à alcools carburants

par

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Résumé

Dans la première partie des travaux, on avait fait l'essai de plusieurs combustibles de remplacement pour véhicules routiers en présence des dispositifs électriques que l'on retrouve habituellement dans les réservoirs, telles les pompes à carburant immergées et les capteurs de niveau. Les essais simulaient différentes situations, avec des dispositifs en bon état ou défectueux, à des températures variées. Il s'agissait de déterminer si des étincelles provenant de ces appareils pouvaient enflammer les vapeurs de carburant emprisonnées dans le réservoir et causer une explosion. Les essais ont été effectués avec des mélanges d'air et de carburant saturés et correspondaient à toutes les situations excepté certaines où les réservoirs seraient presque vides.

Dans cette deuxième partie, l'investigation sur l'inflammation par étincelle porte sur les mélanges air-carburants d'hiver (85% méthanol, 13% essence, 2% butane) et des quantités calculées pour simuler un réservoir presque vide. Les résultats tendent à démontrer que la plage des températures auxquelles les vapeurs résiduelles deviennent inflammables serait plus élevée pour ces carburants.

Mots clés: Carburants à base de méthanol, réservoirs de carburant, véhicules routiers, sécurité intrinsèque, explosions.

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Safety of Reduced Liquid Volumes in Fuel tanks of Road Vehicles Using Alcohol Fuels

by

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ABSTRACT

In the first phase of this work, various road vehicle alternative fuels were tested in conjunction with electrical devices normally used in fuel tanks, such as submersible fuel pumps and level sensors. The tests simulated the operation of these devices both under normal and fault electrical conditions at various temperatures. The intent was to determine whether or not sparks from them could ignite the vapours above the fuel in the tank, thereby causing an explosion. These tests were performed using saturated vapour-air mixtures, which corresponds to all situations except where the tank would be nearly empty.

In this phase of the work, the spark ignition investigations involved winter grade (85% MeOH; 13% Gasoline; 2% Butane) fuel-air mixtures, in quantities intended to simulate nearly empty fuel tanks. The results showed a tendency towards an elevation of the explosive temperature range of the vapours remaining in the tank.

KEYWORDS: Methanol fuels, fuel tanks, road vehicles, intrinsic safety, explosions.

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INTRODUCTION

This report is the result of a request received by the Canadian Explosive Atmospheres Laboratory (CEAL) from Transport Canada to further investigate the properties of winter grade methanol fuel. This fuel is said nominally to consist of 85% methanol, 13% gasoline, and 2% butane. This work would add further information to the work already done and reported in Mining Research Laboratories Divisional Report MRL 88-33 (TR).

In the previous work mentioned above, five fuels were assessed, these being:

methanol;
methanol with cetane improver;
winter grade gasoline:
85% methane and 15% gasoline;
85% methane, 13% gasoline and 2% butane.

The apparatus used to assess these fuels consisted of the standard IEC breakflash apparatus (reference 3) which is designed to interrupt a circuit and produce sparks in the presence of an explosive atmosphere. The IEC apparatus was connected to a standard calibration circuit which was used to determine the smallest possible electrical current, for a given fuel and temperature, at which the generated sparks could ignite the surrounding explosive mixture. The standard calibration circuit consisted of a series-connected 24 Vdc regulated power supply, a 95 mH air core inductor, and a resistance decade box for setting the test current.

In a typical test, the IEC apparatus was placed in a constant temperature chamber, operating at a set temperature. The liquid fuel was admitted into the IEC test chamber; then the vapour space above the fuel was stirred by operating the electrode mechanisms without power applied to the electrodes for 40 minutes

before each trial. The volume of liquid fuel admitted to the chamber corresponded to one thirtieth of the free internal volume of the test chamber. This resulted in a saturated vapour-air mixture, with the excess fluid remaining in the bottom of the test chamber.

Power was then applied to the circuit, so as to allow the IEC apparatus to make and break the circuit at least 1280 times at the specified current.

If ignition occurred before 1280 circuit interruptions were made, the test was stopped, and the apparatus was prepared for the next test at the established current and temperature. If ignition did not occur, the apparatus was prepared for the next test at the established current and temperature. If, at a given temperature and current, ignition occurred in three consecutive tests, the mixture was considered as being ignitable. The current was then changed to a different value (with the same temperature), and another set of three tests was made, this process being repeated until the boundary condition (minimum current) was established.

A family of curves was produced as a result of these tests, and forms part of the previous report. These curves, reproduced as Figure 2 in this report, show that for each type of fuel, there is a range of temperatures above and below which explosions cannot occur. Within the temperature range where ignitions are possible, ignition can occur if ignition-capable sparks are present.

Whether or not a spark can ignite a given vapour-air mixture depends on what mechanical mechanism is producing the spark, since some methods are better than others. The IEC apparatus is the most efficient known method of producing sparks. That is, the IEC apparatus can ignite mixtures where no other apparatus can, all other test conditions being the same. This ability to produce

ignitions is achieved through the use of tungsten wire electrodes, which scrape across the surface of a cadmium disc, and separate from it very quickly several times per second, producing the required electrical sparks.

The type of circuit being interrupted also has a significant effect on whether or not ignitions will occur. For example, a current of 110 mA in the inductive circuit described above will ignite a methane-air mixture. But, this same current will be far from capable of igniting a noninductive circuit (a circuit containing resistors, 24 Vdc power source and IEC breakflash only). In fact more than twenty times this current is required before ignition can occur in a resistive circuit.

Additional tests involved connection of the IEC apparatus to fuel pump and level sensing circuits to simulate standard automotive applications, to determine whether these devices would be ignition-capable. The tests indicated that sparks produced as a consequence of fuel pump circuit interruptions in the tank space could indeed ignite the vapours, within a specified temperature range. Level sensing apparatus proved not to be ignition-capable, due to the much lower currents and noninductive circuits.

All the previous work involved the testing of saturated vapour-air mixtures, which simulates all tank conditions except the almost empty state.

This report deals with the special case of the almost empty tank, in which the vapour-air mixture begins to become unsaturated, using 85-13-2 fuel. This report also provides some additional information relative to the curves shown on Figure 2.

METHOD

The method used was essentially the same as used to generate the family of curves described above (see Fig. 2), except

progressively smaller quantities of 85-13-2 fuel were admitted to the test apparatus.

Three curves were generated (see Fig. 1). The first curve in fact involved a saturated mixture, and was used as a check against the results obtained previously. The volume of liquid fuel admitted to the chamber corresponded to approximately 1.75% of the free internal volume of the test chamber. For the second and third curves, the liquid volumes corresponded to approximately 0.75% and 0.5% (respectively) of the free internal volume of the test chamber.

With reference to the 85-15 and 85-13-2 curves on Figure 2, further efforts were made to determine the maximum temperature at which saturated vapours could be ignited, using a 2.2 Chrysler turbo fuel pump in a 12 Vdc circuit. This fuel pump circuit produced large sparks in the IEC apparatus, as it drew over 10 amps whilst pumping water. In each case, the temperature of the test arrangement was gradually increased, usually with 2 °C increments, with ignition trials at each step.

DISCUSSION OF RESULTS - MAXIMUM TEMPERATURE FOR IGNITION WITH HIGH CURRENTS

The high test current effectively would determine the asymptote on the left (rich mixture) side for each curve. As the temperature was gradually increased, it became increasingly difficult to observe whether or not an ignition had occurred, due to the relative weakness of the explosion. In the case of the 85-15 fuel, ignitions were observed up to -4 °C. In the case of the 85-13-2 fuel, ignitions were observed up to approximately -19 °C. These temperatures do correspond with asymptotic projections for the subject curves.

In general, as more and more ignition energy is liberated into an explosive mixture, ignitions of the fuel-air mixture can be obtained within a wider and wider temperature range. If flames, rather than sparks, (such as the flames produced from a pyrotechnic device), could be used as the ignition source, this yet greater ignition energy would be able to initiate combustion of mixtures not generally ignitible with the level of sparking produced by the IEC apparatus.

DISCUSSION OF RESULTS - REDUCED FUEL VOLUMES

The first curve, corresponding to the 1.75% volume ratio and a saturated mixture of 85-13-2 fuel, was used as a check against the previously reported results. There was good correspondence between the curves in that the minimum ignition current for each occurred in the vicinity of -33 °C, and the explosive range for each curve was in the range -20 °C to -40 °C. The minimum ignition energy for the curve generated in the previous work was about 116 mA, whereas the minimum ignition energy for the present work was found to be about 108 mA. This difference in minimum ignition energies was most likely related to an improvement in the sensitivity of the IEC breakflash apparatus, rather than differences between the two batches of fuel used for the tests.

Changes made to the IEC apparatus between the old series of tests and the new ones included a new cadmium disk, a new one-piece dome, and better humidity control in the temperature chamber. Cadmium disks are known to have variable sensitivities, depending on their history of use. The dome is used to contain the explosive mixture and the sparking mechanism of the IEC apparatus. This dome for normal intrinsic safety tests is repeatedly subjected to a high vacuum during the process of chamber purging, and the previous two-piece unit was subject to leaks. This problem was corrected by having a new dome machined from one solid piece of plastic. Better humidity control meant that a more reliable electrical contact could be made between the

brushes of the IEC apparatus and the rotating shafts with which they must remain in contact.

In general, intrinsic safety tests at low temperatures introduce a somewhat greater variability in test results compared to tests conducted at room temperatures. At these reduced temperatures, gastight seals tend to become brittle and leaky, condensation becomes a problem, and electrical contacts tend to become less reliable.

As can be seen in Figure 1, there appears to be a general broadening of the curves as the amount of fuel admitted to the apparatus is reduced. With 7 mL of 85-13-2 fuel in the chamber, the explosive range was found to be from -20 °C to -40 °C. With 3 mL of the same fuel admitted to the chamber, the range appears to be broadened to approximately -12 °C to -35 °C, and with 2 mL the range is again widened to +3 °C to -32 °C. These ranges are very approximate, and for a clearer picture of what is happening, Figure 1 should be consulted.

Examination of the curve will show that as the quantity of fuel admitted to the test chamber is reduced, the resulting curve tends to approach the shape of the 85-15 curve (85% methanol, 15% gasoline), which was determined in the previous work.

The explanation for this effect is as follows. As the volume of fuel admitted to the chamber is lowered, the quantity of butane in the chamber eventually becomes insignificant, leaving only methanol and gasoline in significant proportions. An insignificant quantity is one where the amount present does not have any effect on the outcome of testing. With reference to eq. 4, in mathematical terms it means the denominator element for butane approaches zero and becomes insignificant to the equation result. If we consider the case where the 2% butane component is effectively no longer present in the IEC apparatus, the remaining

fuel consists of 85 parts methanol and 13 parts gasoline. This corresponds, on a percentage basis, to 87% methanol and 13% gasoline, which is not far from the 85-15 fuel already assessed in the previous work. The amounts of methanol and gasoline in the chamber are still sufficient to produce saturated concentrations of their respective vapours.

This argument can be extended further. If the quantity of fuel in the chamber is decreased again, so that the gasoline fraction is so small as to be insignificant, the only component left that will determine the explosive characteristics of the vapour will be methanol. This means that the curve would again be shifted to coincide with the previously determined methanol curve, resulting in a shift of the explosive range to warmer temperatures.

To check this hypothesis, some further analysis was made. The intent of the calculation was to determine what percentage of butane vapour is present in the test atmosphere, at -20 °C, using 2 mL of the 85-13-2 fuel. Butane vapours in air, at room temperature and atmospheric pressure, according to the CRC Handbook of Chemistry and Physics, have an approximate explosive range of 2% to 8% by volume. If the concentration of butane vapours in air for our test mixture are found to be approximately 2% by volume or less, the butane concentration is bordering on being unignitible, based on the above limits of flammability for butane. This would also show that a transition is taking place, in that the ignition characteristics of the mixture are going from that of the 85-13-2 fuel to those of the 85-15 fuel.

With 2 mL of 85-13-2 fuel in the test chamber, and assuming none of the butane has boiled off during storage and transfer of the fuel to the test chamber, the volume of liquid butane in the IEC apparatus is 2% times 2 mL, which equals 0.04 mL liquid butane. This liquid volume would instantaneously evaporate inside the IEC apparatus, because the butane fraction would be nowhere near the

saturated concentration. According to the ideal gas law, the vapour concentration would be calculated according to the following formula:

$$x = \frac{100 \cdot d \cdot R \cdot T \cdot v}{P \cdot V_c \cdot W} \qquad \text{-----(1)}$$

where x is the butane vapour concentration in air, by volume expressed as a percentage;
d is the density of butane in g/mL;
R is the ideal gas constant = 0.08206;
T is temperature in °K (°K = 273 + °C);
v is the admitted volume of liquid butane in litres;
P is the chamber pressure in atmospheres;
V_c is the chamber volume;
W is the molecular weight of butane, in g per mole.

Plugging in the appropriate numbers yields a butane vapour concentration of 2.14% by volume. This shows that the butane concentration is bordering on the lower explosive limit for butane in air. This is approximate, however, since the vapours from the gasoline and the methanol will displace some of the air in the chamber, changing the effective ratio of butane to air to a somewhat more rich concentration.

A similar mechanism is taking place if one considers the curves for gasoline, methanol, and the 85-15 fuels.

Where a blend of liquid fuels is involved, the total vapour pressure in the chamber is determined by Raoult's Law (applicable to miscible fluids):

$$P_{total} = x_1p_1 + x_2p_2 + x_3p_3 + \ldots + x_np_n \qquad \text{----- (2)}$$

where x_n is the mole fraction for component n
p_n is the partial pressure for component n

In the case of the 85-15 fuel, both constituents contribute some vapour to the atmosphere above the liquid, up to the saturated limit for each component at the specified temperature. For example, at a given temperature, if the vapour pressure times

mole fraction of liquid no. 1 is 100 Torr[1], and the vapour pressure times mole fraction of liquid 2 is 200 Torr, then the total vapour pressure exerted by the mixture will be 300 Torr, or 39.5% by volume[2] at one atmosphere. The balance will be air. This example assumes ideal gas behaviour and a chamber which is essentially closed, but allowed to be vented to atmosphere, to maintain the one atmosphere ambient pressure in the chamber.

First taking into consideration the case of methanol at +10 °C, which is the approximate boundary temperature between ignitibility and non-ignitibility (on the lean side) for the saturated mixture, we use the following formula to determine the theoretical vapour concentration.

$$\log_{10} p = -\frac{0.05223 \cdot a}{T} + b \qquad \text{-----(3)}$$

where p is the pressure in Torr;
T is the temperature in °K;
a is a constant for the substance of interest;
b is a constant for the substance of interest.

Using the appropriate numbers for methanol, as listed in the CRC Handbook of Chemistry and Physics, the saturated vapour pressure of methanol at this temperature is 53.5 Torr, or about 7% by volume. This corresponds very well with the published lower explosive limit for methanol, which is 6.7% by volume in air. The 10 °C temperature is the lower concentration for the methanol, since as the temperature is reduced, a leaner mixture due to the reduced vapour pressure is produced. A check of the upper explosive limit showed that the vapour concentration of methanol at 30 °C was about 20 % by volume. Although this does not show good correlation with the published (Reference 2) upper explosive

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[1] 1 mm Hg = 1 Torr; 1 atmosphere pressure = 760 Torr;

[2] The partial pressure divided by the total pressure yields the volumetric vapour concentration, assuming ideal behaviour.

limit figure of 36% for methanol, the amount of energy used to ignite the rich mixture may be larger than the IEC apparatus can produce. The curve for methanol on the rich side does not rise as steeply as it does the lean side, so the boundary temperature is not as clearly defined. The published figure of a UEL (upper explosive limit) of 36% for methanol was also probably determined using test methods described in Reference 4 which are not directly applicable to the results obtained with the IEC apparatus. The published 36% figure was obtained when the flames were travelling upward; the UEL for horizontal propagation in Reference 4 was 30%, and for downward travel of the flame the UEL was found to be 26%, with all these tests having been done at 60 °C. This elevated test temperature would also have had the effect of increasing the observed UEL for methanol at that temperature.

It is not possible to use eq. (3) for gasoline, since gasoline is a complex blend of a number of hydrocarbons. However, at approximately -30 °C, the gasoline vapour-air mixture is already too rich to be ignitible. As the temperature is increased, the partial pressure of gasoline vapour in air also increases, producing an ever richer mixture of gasoline vapours and air. Since the IEC chamber is operated effectively at one atmosphere, the air volume in the chamber decreases as the increasing amount of gasoline vapours displace the air, with increasing temperature. This same effect occurs in the case of the 85-15 fuel, since adequate gasoline is present to provide saturated gasoline-air vapours.

There comes a point where the ratio of methanol vapour in the 85-15 fuel to the remaining air in the chamber is such that the two once again are in a ratio which allows the mixture at that temperature to be explosive. This accounts for the intermediate position of the 85-15 fuel shown in Figure 2, relative to the

curves for its constituent parts, these being methanol and gasoline respectively.

Considering the case of gasoline only, as the quantity of liquid fuel in the tank is reduced, a point will eventually be reached for any practical temperature, where the vapours above the liquid are no longer in the saturated state. At this point, there will no longer be any liquid in the tank; all the liquid will have evaporated into the atmosphere inside the tank. Explosive vapour-air concentrations are certainly possible under these non-saturated concentrations at any temperature. The amount of liquid gasoline required to form an explosive mixture can be determined by knowing the vapour pressure characteristics of the gasoline, and its explosive range.

More generally, the limits of flammability of a mixture of flammable gases and vapours, as discussed in Reference 4, are expressed by Le Chatelier's Law:

$$L = \frac{100}{\frac{p_1}{N_1} + \frac{p_2}{N_2} + \frac{p_3}{N_3} + \ldots + \frac{p_n}{N_n}} \qquad \text{-----(4)}$$

Where p_n is respectively the percentage of each of the flammable components, such that $p_1 + p_2 + p_3 + \ldots = 100$, noting that nonflammables, such as oxygen, nitrogen, etc. are not counted. The terms N_n represent the flammable limits (upper or lower) of the individual components. This formula may be used for the calculation of the upper explosive limit of a gas or vapour mixture as well as the lower explosive limit, simply by using the appropriate terms in N_n. Reference 4 does caution that this formula may not be accurate for some mixtures, although for the purposes of this paper, the formula should be acceptably accurate (within ±15%), based on work reported in Reference 4 (pp 125).

CONCLUSIONS

Fuel tanks which are nearly empty tend to produce a greater explosion hazard than tanks in which saturated vapour concentrations are maintained. In general, the limits of flammability of the remaining vapours tend to move towards warmer temperatures, and in some cases become distributed over a wider temperature range. Since warmer temperatures do generally occur with a greater probability (even in Canada), the probability of the attendant hazard occurring correspondingly increases. Where electrical sparks are produced under fault conditions, such as in vehicle crashes, this may become an important factor.

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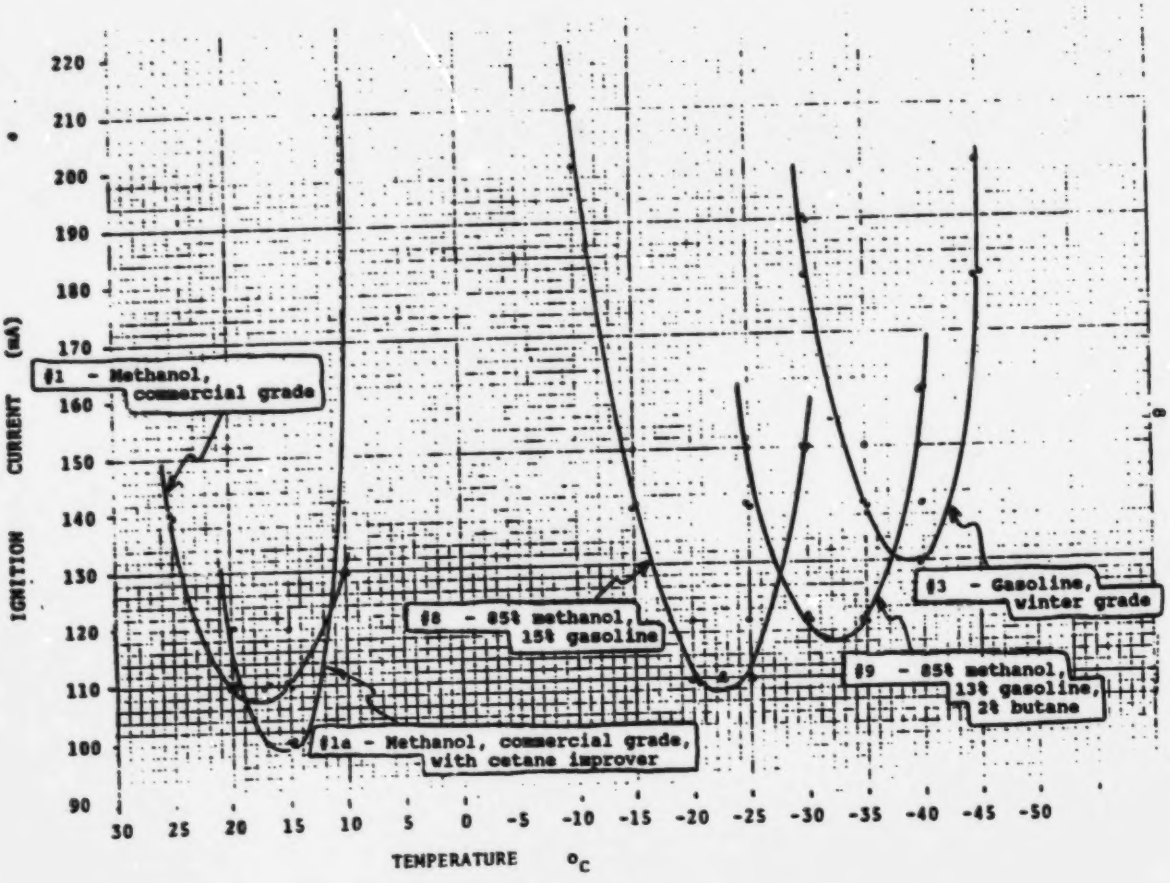
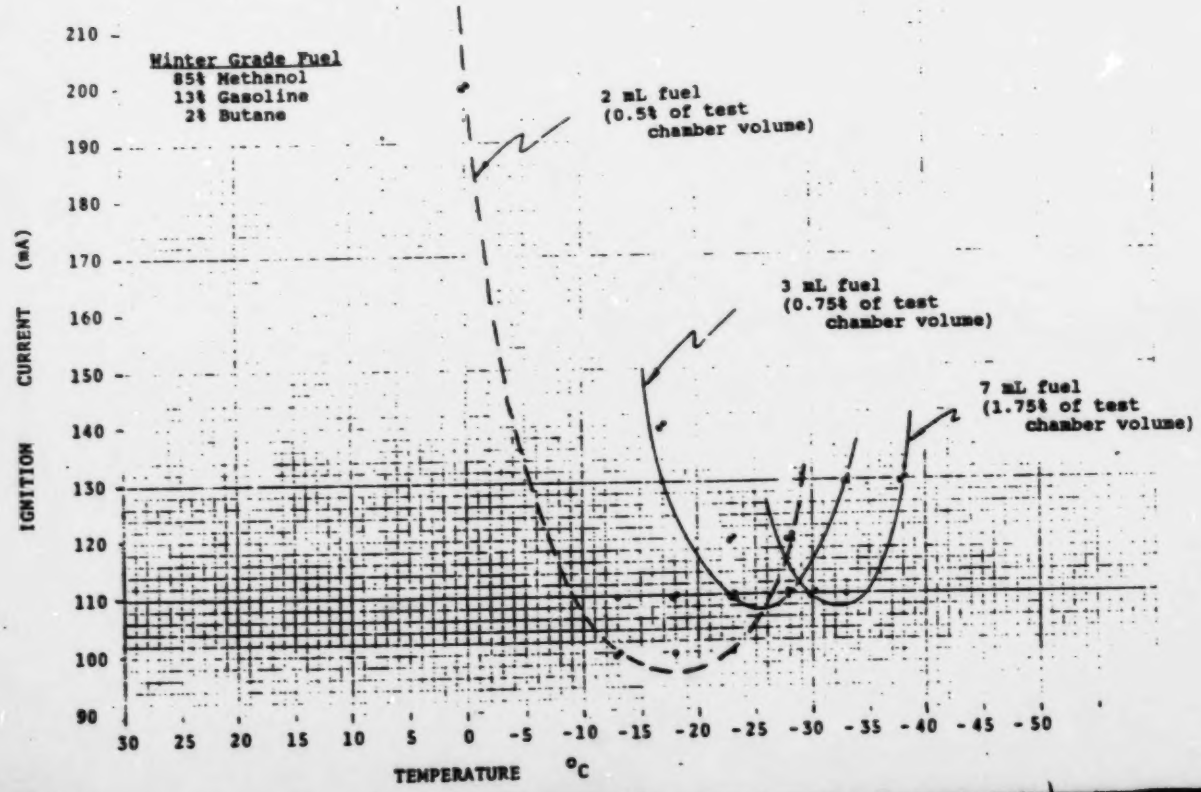

IGNITION CURRENT (mA)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
#1 - Methanol, commercial grade
#8 - 85% methanol, 15% gasoline
#3 - Gasoline, winter grade
#9 - 85% methanol, 13% gasoline, 2% butane
#1a - Methanol, commercial grade, with cetane improver
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
TEMPERATURE °C

Figure - 2


Winter Grade Fuel
85% Methanol
13% Gasoline
2% Butane
2 mL fuel (0.5% of test chamber volume)
3 mL fuel (0.75% of test chamber volume)
7 mL fuel (1.75% of test chamber volume)
IGNITION CURRENT (mA)
210
200
190
180
170
160
150
140
130
120
110
100
90
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
TEMPERATURE °C

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